

RAPID-IMPREGNATION SIZED GLASS STRANDS FOR THE
REINFORCING OF POLYMERS

The invention relates to glass strands coated with a
5 sizing composition which are intended for the
reinforcing of organic materials of the polymer type.

It also relates to the sizing composition used to coat
said strands, to the composites incorporating these
10 strands and to the use of the sized strands in the
manufacture of articles by molding.

Glass strands used for reinforcing are generally
produced industrially from streams of molten glass
15 flowing from the multiple orifices of a spinneret.
These streams are drawn mechanically in the form of
continuous filaments and are then gathered together
into base strands, which are subsequently collected,
for example by winding off on a rotating support.
20 Before they are gathered together, the filaments are
coated with a sizing composition by passing over a
suitable device, such as coating rolls.

The sizing composition proves to be essential in
25 several respects.

During the manufacture of the reinforcing strands, the
sizing composition protects the glass filaments from
the abrasion which occurs when the latter rub at high
30 speed over the various members which are used to guide
them and to collect them. It also establishes bonds
between the filaments, which makes it possible to give
cohesion to the strand. As the strand is thus rendered
more integral, it is easier to handle, in particular
35 during weaving operations, and untimely breakages are
avoided.

During the manufacture of composite materials, the
sizing composition promotes the wetting and

impregnation of the glass strands by the matrix to be reinforced, which matrix is generally employed in the form of a more or less fluid resin. The mechanical properties of the final composite are for this reason
5 markedly improved.

The materials to be reinforced can combine with the glass strands in various forms: continuous or cut strands, mats of continuous or cut strands, fabrics,
10 and the like.

The composites which incorporate cut glass strands can be obtained, inter alia, by the "contact molding" technique, which consists in coating the inside of an
15 open mold, without a countermold, with resin to be reinforced and glass strands of variable length. In the specific process of "molding by simultaneous spraying", the resin and the cut strands are sprayed together onto the inside walls of the mold by means of a "spray gun"
20 comprising an incorporated cutter capable of severing the strands drawn off from one or more wound packages, generally provided in the form of rovings, and of a device which makes it possible to atomize the resin, for example fed via a pneumatic pump. This simple and
25 adjustable process is particularly suited to the one-off or short-run production of components based on thermosetting polymers belonging to the family of the polyesters or epoxides.

30 The quality of the composites obtained by this process depends largely on the properties introduced by the glass strands and thus on the size which coats them. The target is in particular to obtain compositions giving a size which can be easily wetted or impregnated
35 at the surface by the resin in order to provide close contact between the strands and the resin and to thus obtain the expected mechanical reinforcing properties.

It is also desired for these compositions to be

compatible with rapid processing, in particular for the strand/resin mixture which is sprayed onto the mold in the form of overlapping strips to be able to be spread out uniformly. The subsequent rolling stage, intended
5 to remove the air bubbles and to provide better distribution of the strands in the resin, should also be of short duration.

Furthermore, it is necessary for the sizing composition
10 to have a degree of "incompatibility" with the resin, so as to prevent the strands/resin mixture from forming a compact mass which "collapses" by simple gravity. Nevertheless, the impregnation of the strand by the resin should be sufficiently fast so that the
15 strands/resin mixture can have a satisfactory "conformability", that is to say that it is capable of perfectly matching the shape of the mold.

It is also necessary for the cut strands to retain
20 their integrity and not "to form filaments", namely for them not to burst, with the release of their constituent filaments, both during the cutting and spraying phase and during the rolling/debubbling operation.

25 It is thus seen that such compositions are difficult to develop as the targeted properties are rarely compatible with one another and that it is consequently necessary to make compromises.

30 One of the problems encountered during the implementation of the process for molding by simultaneous spraying of strands and of resin is the short lifetime of the blades with which the spray gun
35 is provided. Although they are made of hard steel, the blades of the cutter have a tendency to rapidly wear out on contact with the glass, which leads to "false cuts" and the formation of cut strands with a length greater than that desired. Depending upon the number of

blades, their degree of wear and the position which they occupy on the cutter, it is possible to obtain a mixture of strands with a length corresponding to a whole multiple of the expected length. The false cuts
5 result in an unevenness in the carpet and in poor "conformability" of the cut strands/resin mixture in the mold. In addition, the need to have to replace the old blades at relatively short intervals also results in an increase in the cost of the components.

10

Sized glass strands suited to this type of molding, having an improved ability to be cut, are already known.

15 In FR-A-2 755 127, the strands are coated with a composition which comprises, in addition to adhesion agents capable of providing the sizing function, the combination of an aminosilane and of an unsaturated silane.

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In WO-A-02/059055, the sizing composition coating the glass strands combines at least one bissilane and at least one unsaturated monosilane chosen from vinylsilanes and (meth)acrylosilanes.

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There exists a need to have available a sizing composition which makes it possible to meet current productivity standards, which require having available strands which can be rapidly impregnated by the resin,
30 without, however, affecting the other properties of the strand, and which exhibit a high ability to be cut, making it possible to increase the longevity of the cutting blades while producing the least possible amount of short fibers.

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The aim of the present invention is thus to provide a sizing composition for reinforcing strands, which are intended in particular for open mold molding and more particular for molding by simultaneous spraying of

glass strands and of resin, which makes it possible to have rapid impregnation of the strands by the resin and an improved ability to be cut with limited production of short fibers.

5

A subject-matter of the invention is glass strands coated with an aqueous composition which combines, as film-forming adhesion agents, at least one polyester, at least one polyvinyl acetate and at least one polyurethane.

In the present invention, the term "glass strands coated with a sizing composition" is understood to mean glass strands "which have been coated with a sizing composition which comprises ...", that is to say not only glass strands coated with the composition in question as they are obtained at the immediate outlet of the sizing member or members but also these same strands after they have been subjected to one or more other treatments. Mention may be made, as examples of such treatments, of the drying operations targeted at removing the solvent from the composition and the treatments resulting in the polymerization/crosslinking of some constituents of the sizing composition.

25

Still within the context of the invention, the term "strands" should be understood as meaning the base strands resulting from the gathering together under the spinneret of a multitude of filaments and the products derived from these strands, in particular the assemblages of these base strands into rovings. Such assemblages can be obtained by simultaneously reeling off several wound base strand packages and by then gathering them together into slivers which are wound off onto a rotating support. It can also be "direct" rovings with a count (or mass length) equivalent to that of the assembled rovings obtained by gathering together filaments directly under the spinneret and winding onto a rotating support.

Still according to the invention, the term "aqueous sizing composition" is understood to mean a sizing composition in the form of a solution in which the liquid phase is composed to 97% by weight of water, preferably 99% and better still 100%, the remainder being composed, if appropriate, of one or more essentially organic solvents which can help in dissolving some constituents of the sizing composition.

10

In accordance with the invention, the sizing composition comprises, as film-forming adhesion agents, the blend of at least one polyester, of at least one polyvinyl acetate and of at least one polyurethane.

15

The polyester makes it possible to obtain rapid impregnation by the resin and good conformability of the strands/resin mixture in the mold. It also confers stiffness on the glass strands.

20

The polyester is obtained by reaction of polycarboxylic acid(s) and/or of anhydride(s) of these acids and of polyol(s).

25

Preferably, the acid is chosen from saturated, unsaturated or aromatic diacids, such as fumaric acid, isophthalic acid and terephthalic acid, the anhydride is chosen from phthalic anhydride and maleic anhydride, and the polyol is chosen from polyalkylene glycols, such as ethylene glycol and propylene glycol, aromatic polyols, such as bisphenol A or F, and novolaks.

30

Preference is given to the polyesters obtained by reaction of phthalic or maleic anhydride and of bisphenol A or F, and of phthalic and maleic anhydrides and of propylene glycol.

35

Generally, the polyester exhibits a molecular weight which varies from 4000 to 17 000 g/mol.

The amount of polyester generally represents 50 to 80% of the solid materials of the composition, preferably 50 to 70%.

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The polyvinyl acetate is important in achieving the required level of cutting.

10 The molecular weight of the polyvinyl acetate is generally less than 80 000 g/mol, preferably less than 70 000 g/mol and better still it is between 40 000 and 65 000 g/mol.

15 The amount of polyvinyl acetate used generally represents 10 to 40% by weight of the solid materials of the sizing composition, preferably 20 to 30%. When the amount represents less than 10% of the solid materials, the ability to be cut is not satisfactory and, when it exceeds 40%, the impregnation of the
20 strands is inadequate.

The polyurethane renders the strand more integral and improves its ability to be cut. It also acts as a lubricant.

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The polyurethane is chosen from the polyurethanes resulting from the reaction of at least one polyisocyanate and of at least one polyol comprising an aliphatic and/or cycloaliphatic chain.

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Preferably, the polyurethane has a molecular weight of less than 20 000 g/mol, preferably of between 4000 and 15 000 g/mol.

35 The amount of polyurethane used generally represents 8 to 15% by weight of the solid materials of the sizing composition, preferably 8 to 10%.

Preferably, the sum of the contents by weight of

polyester, of polyvinyl acetate and of polyurethane represents at least 90%, preferably at least 95%, of the solid materials of the sizing composition.

5 In addition to the abovementioned components which participate essentially in the structure of the size, the sizing composition can advantageously comprise one or more other components (hereinafter denoted as "additives"). The sizing composition can thus comprise
10 a lubricating agent in an amount which can represent up to 5% by weight of the solid materials of the sizing composition.

In addition to this role of protecting the filaments
15 from mechanical abrasion, the lubricant contributes to limiting the formation of short fibers, to increasing the stiffness of the strand and to preventing adhesive bonding of the wraps on the wound base strand packages.

20 Generally, this agent is chosen from cationic compounds of the polyalkyleneimide type and nonionic compounds of the esters of fatty acids and of poly(alkylene glycol)s/poly(oxyalkylene) type, such as polyethylene glycol monolaurate, or of the poly(oxyalkylenated)
25 fatty amides type, such as polyoxyethylenated hydrogenated tallow amides.

The sizing composition can also comprise at least one coupling agent which makes it possible to attach the
30 size to the surface of the glass filaments. The coupling agent is generally chosen from silanes, such as γ -glycidoxypropyltrimethoxysilane, γ -acryloyloxypropyltrimethoxysilane, γ -methacryloyloxypropyltrimethoxysilane, poly(oxyethylene/oxypropylene)tri-
35 methoxysilane, γ -aminopropyltriethoxysilane, vinyltrimethoxysilane, phenylaminopropyltrimethoxysilane or styrylaminoethylaminopropyltrimethoxysilane, siloxanes, titanates, zirconates, in particular of aluminum, and mixtures of these compounds. Preferably, silanes are

chosen.

Advantageously, the composition comprises at least two coupling agents, at least one of which is an
5 unsaturated silane and the other of which is an aminosilane. A particularly advantageous combination comprises at least one silane including an acrylic or methacrylic functional group and an aminosilane chosen from bis(γ -trimethoxysilylpropyl)silane and bis(γ -
10 triethoxysilylpropyl)silane. In particular, by adjusting the ratio by weight of the unsaturated silane to the aminosilane, it is possible to regulate the amount of "oversize" to be applied to the base strands, as is indicated later. The ratio generally varies from
15 1:1.5 to 1:6, preferably from 1:2 to 1:5. The higher the ratio, the lower the amount of oversize to be deposited.

The amount of coupling agent generally varies from 1 to
20 6% by weight of the solid materials of the sizing composition, is preferably greater than 1.5% and is generally of the order of 2%.

It is also possible to introduce, as additive, an
25 antistatic agent, such as lithium chloride, in an amount representing less than 5% by weight of the solid materials of the sizing composition.

The glass strands coated with the sizing composition in
30 accordance with the invention exhibit a loss on ignition of less than 2.2%, preferably of greater than 1% and better still of between 1.0 and 1.45%.

Generally, the glass strands in accordance with the
35 invention are provided in the form of wound base strand packages which are subjected to a heat treatment. This treatment is intended essentially to remove the water introduced by the sizing composition and, if appropriate, makes it possible to accelerate the

crosslinking of the film-forming adhesion agents. The conditions of the treatment can vary according to the weight of the wound package. The drying is generally carried out at a temperature of the order of 110 to 140°C for several hours, preferably 12 to 18 hours.

As has already been said, the base strands thus obtained are generally removed from the wound package and combined with several other base strands into a sliver which is subsequently wound onto a rotating support to form a roving. The "oversize" application of a composition including a cationic antistatic agent of the quaternary ammonium salt type to the strands makes it possible to reinforce the ability of the strands to be cut. Consequently, the deposition of the abovementioned composition on the base strands, after removing from the wound package and gathering together to form the sliver, contributes to improving the ability to be cut and consequently increases the lifetime of the blades. The strands are preferably coated with an aqueous composition comprising 20 to 35% by weight of cetyltrimethylammonium chloride, preferably of the order of 25% by weight.

The amount of "oversize" deposited generally represents 0.02 to 0.2% by weight of the strand, preferably 0.05 to 0.10%.

The strands coated with the sizing composition according to the invention can be composed of glass of any nature provided that it is capable of being fiberized, for example of E, C or AR (alkali-resistant) glass or glass with a low level of boron (less than 5%). E glass and glass with a low level of boron are preferred.

These same strands are composed of filaments with a diameter which can vary within a wide range, for example 9 to 17 μm , preferably 11 to 13 μm .

The strands advantageously have a count of between 30 and 160 tex, preferably 40 and 60 tex. Such cut glass strands are evenly and homogeneously distributed within the resin, which makes it possible to have
5 reinforcement of excellent quality.

Another subject-matter of the invention is the sizing composition capable of coating said glass strands, which composition is characterized in that it comprises
10 an aqueous blend of at least one polyester, of at least one polyvinyl acetate and of at least one polyurethane as are defined above.

The sizing composition is an aqueous blend comprising
15 the constituents below in the following contents by weight, expressed as percentages of the solid materials:

- 50 to 80% of at least one polyester, preferably 50 to 70%,
- 20 • 10 to 40% of at least one polyvinyl acetate, preferably 20 to 30%,
- 8 to 15% of at least one polyurethane, preferably 8 to 10%,
- 0 to 5% of at least one lubricating agent,
- 25 • 1 to 6% of at least one coupling agent, preferably equal to or greater than 1.5%.

Advantageously, the sizing composition comprises between 5 and 15% by weight of solid materials,
30 preferably between 6 and 11%. Advantageously, the liquid phase is composed to 100% of water.

Another subject-matter of the invention is also the composites comprising the glass strands coated with the
35 sizing composition. Such composites comprise at least one thermosetting material, preferably a polyester, a vinyl ester, an acrylic polymer, a phenolic resin or an epoxy resin, and glass strands composed, in all or part, of glass strands in accordance with the

invention.

The level of glass within the composite is generally between 20 and 45% by weight and preferably between 25
5 and 35%.

In addition to their advantages related to the processing by molding (rapid rate of impregnation and good ability to be cut, combined with the limited
10 formation of short fibers), the glass strands confer, on the composites which include them, better resistance to aging, in particular in a moist environment.

A further subject matter of the invention is the use of
15 the glass strands coated with the sizing composition for the production of components by the open mold molding technique, in particular by simultaneous spraying of said strands and of resin.

20 Another subject matter of the invention is the use of said glass strands for the production of pipes by the centrifuging technique, which consists in simultaneously spraying the strands and a resin into a rotating mold, the impregnation of the strands being
25 carried out by virtue of the centrifugal force.

The following examples make it possible to illustrate the invention without, however, limiting it.

30 EXAMPLE 1 (COMPARATIVE)

A sizing composition is prepared in the form of an aqueous solution comprising, as % by weight of the solid materials:

- 35 • film-forming adhesion agents
- polyvinyl acetate⁽¹⁾; molecular weight 50 000 60.1
 - vinyl acetate/N-methylolacrylamide copolymer⁽²⁾ 21.9

- coupling agents
 - diaminosilane⁽³⁾ 1.3
 - vinyltriethoxysilane⁽⁴⁾ 2.1
 - plasticizer
 - 5 - mixture of diethylene glycol dibenzoate and of propylene glycol dibenzoate⁽⁵⁾ (50:50 ratio by weight) 9.8
 - lubricants
 - polyethylene glycol 400 monolaurate⁽⁶⁾ 4.1
 - 10 - polyethyleneimide comprising free amide functional groups⁽⁷⁾ 0.7
 - water: amount sufficient to give 100 ml of sizing composition.
- 15 The sizing composition is prepared in the following way:
- The alkoxy groups of the silane⁽³⁾ and silane⁽⁴⁾ are hydrolyzed by addition of acid to an aqueous solution
- 20 of this silane kept stirred.
- The other constituents are subsequently introduced, still with stirring, and the pH is adjusted to a value of 4 ± 0.2 , if necessary.
- 25 The sizing composition is used to coat, in a known way, filaments of E glass with a diameter of approximately 12 μm drawn from glass streams flowing from the orifices of a spinneret, the filaments subsequently
- 30 being gathered together in the form of wound base strand packages with a count equal to 60 tex.
- The wound package is dried at 130°C for 12 hours.
- 35 The base strands extracted from 7 wound packages are coated with an aqueous solution comprising 25% by weight of cetyltrimethylammonium chloride (amount deposited on a dry basis: 0.05%).

The strand unwound from the roving is inserted into a cutting device comprising two blades, one made of hard steel and the other made of rapidly wearing "soft" steel (heat treatment at 550°C), and equipped with strength and temperature sensors. The cutting, carried out at 20°C under a relative humidity of 50%, is adjusted in order to form cut strands with a length of 50 mm. The ability to be cut is measured by the weight of the glass strands which can be cut until the appearance of strands with twice the length (2 x 50 mm). The value 1 is assigned to the weight of cut strands obtained, which value is used here as reference value for measuring the ability to be cut.

15 EXAMPLE 2

The preparation is carried out under the conditions of example 1, modified in that the sizing composition comprises, as % by weight of the solid materials:

- 20 • film-forming adhesion agents
 - polyester⁽⁸⁾ 60.5
 - polyvinyl acetate⁽¹⁾ 22.5
 - polyurethane⁽⁹⁾ 10.0
- coupling agents
- 25 - (γ -methacryloyloxypropyl)triethoxysilane⁽¹⁰⁾ 3.2
- lubricating agent
 - polyethyleneimide polyamide salt⁽¹¹⁾ 0.8
 - quaternary ammonium derivative⁽¹²⁾ 3.0
- water: amount sufficient to give 100 ml of sizing composition.
- 30

The sizing composition has a solids content of 6.6%.

The following properties are evaluated on the strand resulting from the roving:

- the loss on ignition, in %, is measured under the conditions of standard ISO 1887,
- the short fibers are measured by reeling off the strand over a device composed of 6 tension rollers,

at the rate of 93 m/min. The device is placed in a conditioned room at 20°C and 50% relative humidity. The short fibers are defined by the amount of fibrils, in mg, obtained after reeling off a weight
5 of strand of 1 kg.

The values of the loss on ignition, of the short fibers and of the ability to be cut appear in table 1.

10 **EXAMPLE 3**

The preparation is carried out under the conditions of example 2, modified in that the content of cetyltrimethylammonium chloride deposited on the base
15 strands is equal to 0.10%.

The composition has a solids content of 6.6%.

The values of the loss on ignition, of the short fibers
20 and of the ability to be cut appear in table 1.

EXAMPLE 4 (COMPARATIVE)

The preparation is carried out under the conditions of
25 example 2, modified in that the film-forming adhesion agents are composed solely of polyester⁽⁸⁾ in a content of 93%.

The sizing composition has a solids content of 6.5%.
30

The values of the loss on ignition, of the short fibers and of the ability to be cut appear in table 1.

EXAMPLE 5 (COMPARATIVE)

35 The preparation is carried out under the conditions of example 2, modified in that the sizing composition comprises the following film-forming adhesion agents, as % by weight of the solid materials:

- film-forming adhesion agents
 - polyester⁽⁸⁾ 88.4
 - polyurethane⁽⁹⁾ 4.8
- coupling agents
 - 5 - (γ-methacryloyloxypropyl)triethoxysilane⁽¹⁰⁾ 3.1
- lubricating agent
 - polyethyleneimide polyamide salt⁽¹¹⁾ 0.8
 - quaternary ammonium derivative⁽¹²⁾ 2.9
- water: amount sufficient to give 100 ml of
10 sizing composition.

The sizing composition has a solids content of 6.8%.

15 The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

EXAMPLE 6 (COMPARATIVE)

20 The preparation is carried out under the conditions of
example 2, modified in that the sizing composition
comprises the following film-forming adhesion agents,
as % by weight of the solid materials:

- film-forming adhesion agents
 - polyester⁽⁸⁾ 59.2
 - 25 - polyvinyl acetate⁽¹⁾ 29.6
- coupling agents
 - (γ-methacryloyloxypropyl)triethoxysilane⁽¹⁰⁾ 3.1
- plasticizer
 - mixture of diethylene glycol dibenzoate
30 and of propylene glycol dibenzoate⁽⁵⁾
(50:50 ratio by weight) 4.4
- lubricating agent
 - polyethyleneimide polyamide salt⁽¹¹⁾ 0.8
 - quaternary ammonium derivative⁽¹²⁾ 2.9

35 The sizing composition has a solids content of 6.8%.

The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

EXAMPLE 7 (COMPARATIVE)

5 Use is made of glass strands coated with a size which
are suitable for the preparation of composite
components by molding by simultaneously spraying. These
strands are sold by PPG under the reference 6313.

10 The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

EXAMPLE 8

15 The preparation is carried out under the conditions of
example 2, modified in that the sizing composition
comprises 0.2% of lubricating agent⁽¹¹⁾ and is devoid of
antistatic agent⁽¹²⁾.

20 The sizing composition has a solids content of 6.4%.

The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

EXAMPLE 9

25 The preparation is carried out under the conditions of
example 3, modified in that the sizing composition
comprises 0.2% of lubricating agent⁽¹¹⁾.

30 The sizing composition has a solids content of 6.94%.

The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

EXAMPLE 10

35 The preparation is carried out under the conditions of
example 2, modified in that the sizing composition
comprises, as % by weight of the solid materials:

	- polyester ⁽⁸⁾	54.0
	- polyvinyl acetate ⁽¹⁾	24.0
	- polyurethane ⁽⁹⁾	10.0
	- silane ⁽¹⁰⁾	1.7
5	- lubricating agent ⁽¹¹⁾	0.3

The sizing composition has a solids content of 8.4%.

The values of the loss on ignition, of the short fibers
10 and of the ability to be cut appear in table 1.

EXAMPLE 11

The preparation is carried out under the conditions of
15 example 2, modified in that, in the sizing composition,
the polyester⁽⁸⁾ is replaced by the polyester⁽¹³⁾.

The sizing composition has a solids content of 8.3%.

20 The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

EXAMPLE 12

25 The preparation is carried out under the conditions of
example 2, modified in that the sizing composition
comprises the following coupling agents, as % by weight
of the solid materials:

	- polyester ⁽⁸⁾	61.8
30	- polyvinyl acetate ⁽¹⁾	23.0
	- polyurethane ⁽⁹⁾	10.2
	- unsaturated silane ⁽¹⁰⁾	0.8
	- bis(triethoxysilylpropyl)amine ⁽¹³⁾	4.0
	- lubricating agent ⁽¹¹⁾	0.2

35

The sizing composition has a solids content of 8.6%.

The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

EXAMPLE 13

5 The preparation is carried out under the conditions of
example 12, modified in that the content of
cetyltrimethylammonium chloride deposited on the base
strands is equal to 0.10%.

The ability to be cut is given in table 1.

10

EXAMPLE 14

15 The preparation is carried out under the conditions of
example 12, modified in that cetyltrimethylammonium
chloride is not deposited on the base strands.

The values of the loss on ignition, of the short fibers
and of the ability to be cut appear in table 1.

20 **EXAMPLES 15 TO 17**

The strands obtained according to examples 2 and 10
(examples 15 and 16) and according to comparative
example 7 (example 17) are used to manufacture
25 composite components by the technique of molding by
simultaneous spraying under the following conditions:

- the glass strand removed from the roving is
introduced into a spray gun (Vénus from Matrasur)
which makes it possible to cut it and to spray it
30 simultaneously with an unsaturated polyester resin
(Enydyne D05 4500 TY, sold by Cray Valley) with a
viscosity equal to 4.5 dPa·s at 25°C, with high
reactivity and thixotropic,
- the mold into which the cut strands and the resin
35 are sprayed is a mold in the form of a staircase
which comprises a vertical wall with a height of
1 m, then a stair with a depth of 0.20 m and a
height of 0.2 m, and finally a horizontal wall
with a length of 1 m. The horizontal wall

comprises two grooves with a depth of 2 cm which make it possible to evaluate the conformation of the cut strands/resin mixture,

- 5 - the mixture sprayed onto the mold includes 30% by weight of glass and has a mean thickness of the order of 3 mm.

The performances of the cut strands/resin mixture are evaluated for the following parameters:

- 10 - evenness of the carpet
 - vertical wall strength
 - rate of impregnation of the cut strands by the resin.

- 15 The evaluation relating to these parameters is measured visually according to the following scale of values:
1 = very bad; 2 = bad; 3 = fairly good; 4 = good and 5 = very good.

- 20 The performances of the strands are collated in table 2 below:

Table 2

	Ex. 15	Ex. 16	Ex. 17
Strand	Ex. 2	Ex. 10	Ex. 7
Dispersion of the carpet	4.5	4	3.5
Vertical wall strength	2.5	4.5	2
Rate of impregnation	4	4	4

- 25 On reading the table, it is found that the strands according to the invention (examples 2 and 3), which combine a polyester, a polyvinyl acetate and a polyurethane as film-forming adhesion agents, exhibit a better ability to be cut than the strands comprising only one or two of these agents (examples 4 to 6), at an equivalent loss on ignition. The amount of short fibers formed is low, of the same level as for examples 4 to 6 and much lower than that of the strands of
- 30

example 7.

The ability to be cut is improved when the content of "oversize" is greater (example 3).

5

The strands having lower contents of lubricating agent (examples 8 and 9) and of coupling agent (example 10) have a high ability to be cut and moderate production of short fibers.

10

The combination of an unsaturated silane and of an aminosilane makes it possible to obtain strands having a high ability to be cut without oversize (example 14), this ability greatly increasing when the content of oversize increases (examples 12 and 13).

15

Table 2 shows that the strands according to the invention (examples 15 to 17) retain a high rate of impregnation under the conditions of the spraying, equivalent to that of the strands of comparative example 7, with, however, an improved vertical wall strength and evenness of the carpet.

20

These strands obtained in the context of the invention exhibit an excellent compromise between the ability to be cut, the production of short fibers and the conditions of molding by simultaneous spraying of resin.

25

30 EXAMPLES 18 AND 19

The ability of the strand according to example 10 (example 18) to be used to manufacture pipes by the centrifuging technique by simultaneous spraying of cut strands and of resin into a rotating mold is evaluated by comparison with a known strand suitable for this use (sold by PPG under the reference 6428; example 20).

35

The integrity of the strand is measured under the

following conditions: the strand reeled off from a roving is introduced into a Wolfangel 500 cutter, which cuts it and sprays it substantially horizontally onto a vertical wall (cutting rate: 600 m/min; length: 12 mm).

- 5 The integrity of the cut strand is determined visually according to a scale of values ranging from 1 (bad; fluffy appearance) to 5 (very good; no rupturing of the strand).
- 10 The ability to be cut is measured under the conditions of example 1.

	Example 19	Example 20
Integrity	4.5	4.5
Ability to be cut	2.40	0.95

- 15 The strand according to the invention exhibits a markedly improved ability to be cut in comparison with the known strand and an identical integrity.

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- 20 (1) Sold under the reference "Vinamul[®] 8852" by VINAMUL; solids content: 55%
 - (2) Sold under the reference "Vinamul[®] 8828" by VINAMUL; solids content: 52%
 - (3) Sold under the reference "Silquest[®] A 1126" by GESM; solids content: 35%
 - (4) Sold under the reference "Silquest[®] A 151" by GESM; solids content: 98%
 - (5) Sold under the reference "K-Flex[®] 500" by NOVEON; solids content: 100%
 - (6) Sold under the reference "Ensital[®] 4L" by COGNIS; solids content: 100%
 - 25 (7) Sold under the reference "Emery[®] 6717" by COGNIS; solids content: 100%
 - (8) Sold under the reference "Neoxil[®] 954D" by DSM; solids content: 47%
 - (9) Sold under the reference "Neoxil[®] 9851" by DSM; solids content: 33%
 - (10) Sold under the reference "Silquest[®] A 174" by GESM; solids content: 70%
 - (11) Sold under the reference "Emery[®] 6760" by COGNIS; solids content: 100%
 - 30 (12) Sold under the reference "Neoxil[®] AO 5620" by DSM; solids content: 100%
 - (13) Sold under the reference "Filco[®] 350" by COIM; solids content: 45%
 - (14) Sold under the reference "A 1122" by DEGUSSA; solids content: 98%

Table 1

Example	1	2	3	4 (Comp.)	5 (Comp.)	6 (Comp.)	7 (Comp.)	8	9	10	11	12	13	14
Loss on ignition(%)	-	1.30	1.03	1.01	1.20	1.21	1.30	1.28	1.26	1.44	1.37	1.24	-	1.20
Short fibers (mg)	-	8	6	6	6	11	32	11	11	4	5	5	-	3
Ability to be cut	1	1.90	2.15	1.20	1.15	1.20	2.3	2	3.2	2.40	2	6.5	11	2.5